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POLLUTANT TRANSFER BETWEEN AIR, WATER AND SOIL: CRITERIA FOR COMPREHENSIVE POLLUTION CONTROL STRATEGY

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ABSTRACT

Large amounts of pollutants are continuously discharged into air, water or soil – the three domains of the Ecosystem. These domains have mutual interactions in terms of mass transfer, which affect the concentration of these pollutants both temporally and spacially in all domains. The intra-domain interactions that influence the pollutant transfer between air, water and soil may be either due to the bulk phase transfer (e.g., acid rain) or due to interfacial transfer (e.g., pesticide evaporation from soil to air). The mathematical equations based on the general principles of mass transfer such as Fick's Law of Diffusion and Rault's Law, and equilibrium relationships can quantitatively predict the pollutant transfer from one phase to another.

Thus far, our pollution control efforts have been directed at each individual domain without much regard to their effect on the other domains. This has, in some cases, merely shifted the problem instead of solving it. A basic understanding of transfer processes is presented here. The problem of trihalomethanes in water is discussed to support the case for a comprehensive pollution control strategy which makes both technical and economic sense.

INTRODUCTION

Ecosystem is comprised of various interdependent subsystems – air, water, land. All life (micro and macro organisms) including plant, animal and human is also a part of the ecosystem and interacts with other subsystems within the ecosystem.

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Some chemicals are passed from one subsystem to another and go through various changes in form but get regenerated and are cyclic in nature. Carbon, nitrogen, and phosphorous are some examples. There are cycles of chemicals within these cycles which affect the interdependence of these subsystems also. These cycles may (e.g., nitrogen) or may not (e.g., NO_2 photolytic) cross the subsystem boundaries and therefore may or may not affect more than one subsystem in the environment.

In the past we have considered the pollution control of each subsystem separately, without regard to their interdependence. This, in some cases, has led to shifting of the problem from one subsystem to another, and in some cases with more harmful effects in the subsequent subsystem, than in the original subsystem. The pollutants cross the subsystem boundaries by various processes and a fragmented look at one subsystem at a time may not be enough. The acceptable ultimate disposal and treatment of waste is a complex proposition and needs to be looked at, in a comprehensive manner. Resource recovery, waste to food and waste to energy processes may provide solutions of more acceptable nature in the long run even though economically they may not be feasible yet.

The pollutant cycle in nature is outlined in Figure 1. A pollutant, when discharged from a source may go to air (by evaporation), water (by dissolution) or soil (by adsorption). Once in air, water or soil, the pollutant can transfer from one domain to the other as shown in Figure 1. Currently our efforts to curb environmental pollution are directed in the following two areas: 1) reduce the pollution at the source; and 2) control and disperse the pollution that cannot be curbed at the source.

Emission standards and regulations for part 1) are, in general, obtained by calculating backwards from the effects of pollutant on the receptors (man, animal, material, plants, etc.). Some control techniques, both in parts 1) and 2) above, merely disperse or transfer the pollution but the cumulative effect on the receptors remains the same. For example, tall stacks constructed to reduce the pollutant concentration do so at the expense of dispersing the pollutant over larger area. Thus the problem is not really solved but diffused. Control of SO_2 or NH_3 by scrubbing with water produces effluents which if discharged into water cause water pollution. Acid rain transforms air pollution to water and soil pollution.

In this article the interrelationships between various domains – air, water and soil – and a discussion of pollutant transport across the interphase between these domains is provided. Intra-domain (within the same domain) transfer of pollutants is not treated here as this kind of pollutant movement does not shift the problem from one domain to another.

In the final analysis an example of comprehensive control technology is provided for the pollution control of trihalomethanes in water.

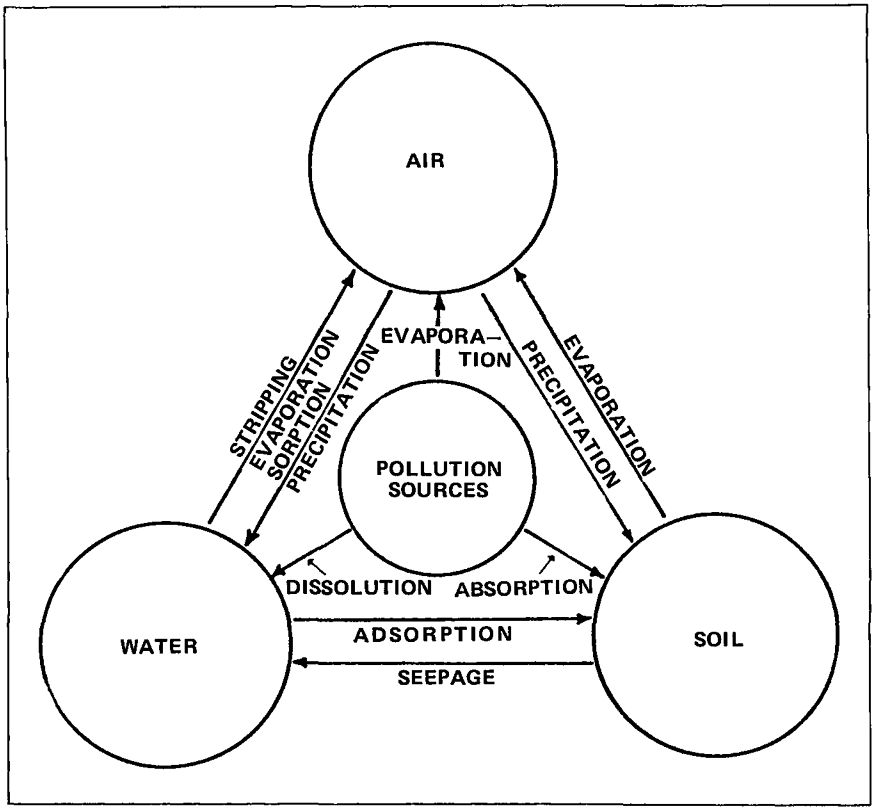


Figure 1. Pollutant cycle in nature.

POLLUTANT TRANSFER ACROSS INTERPHASES

When a substance is introduced into one domain – air, water or soil – it can find its way into the remaining two domains via these two mechanisms: 1) bulk phase transfer or 2) interfacial transfer. An example of bulk phase transfer is precipitation which may carry pollutants in air to water and land. Acid rain is a case in point. Due to combustion processes, U. S. discharges approximately fifty million metric tons of sulfur and nitrogen oxides into the atmosphere [1]. These pollutants are converted into acids via complex ractions, and rain or snow carry them onto the ground where they cause water pollution and material/buliding damage. Crop yields are affected in two ways – one by the direct affect of acidity on the foliage and the other by the indirect effects due to leaching of minerals from soils. Acid rain may result either as wet deposition as described above or by dry deposition which involves the adsorption of SO_2 or NO directly on to particles in the atmosphere. When contacted with rain or snow, they are converted to acids. SO_x and NO_x are the major contributors to the acid rain. In 1977, they combined for over a quarter of the total air pollution in the United States. With the recent shift in combustion fuels from oil to coal (with sulfur) the problem of acid rain may become more significant in the coming years.

Interfacial transfer of pollutants is a result of the driving forces caused by the concentration differences on either side of the interphase. The approach towards equilibrium depends on a number of factors, prominent among them being:

1. ambient conditions (temperature, pressure, turbulence);
2. solubilities – partition coefficients; and
3. vapor pressure of pollutants.

These factors are sometimes interdependent, e.g., vapor pressure and solubility are functions of temperature. Once these factors are known, the relative distribution of the pollutant in either domain may be calculated, based on the approximate thermodynamic relationship such as Henry's or Raults' Law.

Air ⟷ Soil

The transfer of pollutants from air to soil may be a result of either bulk phase transfer or interfacial transfer. Bulk phase transfer, such as acid rain may affect the soil system in the following ways:

1. reduction growth;
2. inhibition of bacterial decomposition;
3. inhibition of nitrogen fixation; and
4. leaching of calcium, magnesium and potassium from leaves and soil.

Minerals and chemicals enter the soil either through parent rock or by atmospheric deposition and are constantly recycled to earth as dead organic matter. This organic matter must first be broken down by bacteria and fungi to convert them to usable form for plants.

Acid rain may disrupt this system of soil regeneration in two ways. Firstly the decay of organic matter could be suppressed by the acid in the rain and secondly nutrients like calcium, magnesium and potassium could be washed rapidly into the ground water thus reducing the mineral store of soil. In addition acid rain could have direct impact on the plant life and growth. The process of photosynthesis has been demonstrated to slow down under acidic conditions. Forest growth and vegetation may be affected both in quality and quantity.

Additionally, damage in the forms of erosion and corrosion have been linked to buildings, automobiles, etc., including damage to irreplaceable historical sculptures and monuments.

The interfacial transfer of chemicals from air to soil surfaces follows the general laws of adsorption. Langmuir, Freundlich type isotherms describe the behavior of this type of pollutant transfer. Many chemical pollutants exist in dispersed phase close to the land surface and can get adsorbed on plants and materials. The reverse problem, however, is of greater significance – the transfer of pollutants from the soil surface.

Presticides, chemical spills and chemical dumps generally involve air-land interphase and hence the transfer of pollutants from land to air. Volatilization of these chemicals essentially depends upon the ambient conditions and the vapor pressure of these pollutants at those conditions [2].

Air ↔ Water

The pollutant transfer is very pronounced between air and water domains. Evaporation of organics from water to air and the transfer of chemicals from air to water via rain and snow are the major paths of air-water pollutant interchange.

Transfer of heavy metals from air to water via acid rain or particle deposition is of great significance in drinking water quality. Recent studies have shown that minute amounts of mercury compounds in rainfall, under acidic conditions, could be converted to toxic methyl mercury, which not only can kill the fish but can also cause serious damage, even death, in very low concentrations if consumed by humans in the form of surviving fish. Runoff and leaching of metals such as aluminum due to acid rain can also cause fish to die.

Chlorinated organics which are formed both in air and water and are suspected carcinogens, can transfer from air to water via preceiptation and from water to air via volatilization.

Particulate matter in a certain size range can settle due to gravitational forces obeying Stokes' law.

When a chemical is distributed between two phases, equilibrium conditions require that the chemical potential or the fugacities of the chemical be equal in the two phases at equilibrium. The resulting concentration of the pollutant in the two phases can be calculated by the use of partition coefficients, relative volatility or Henry's law depending on the situation.

Water ↔ Soil

The problem of soil pollution, in general is different from those of water and air, because the pollution remains there for a long period of time. The soil matrix, in past, has become a "deposit site" or solid and hazardous liquid waste. The soil has the capability of treating the numerous hazardous chemicals by physical and biochemical processes. Under ideal conditions it transforms and stabilizes the chemical into innocuous components. However, a dynamic equilibrium must be maintained; and the capacity of soil to become the first receptacle is not unlimited.

Soils are composed of solid-organics and inorganics, gaseous phase and moisture. The size and distribution of particulate matter varies. The quality of each size fraction determines the surface area. Some of the soils like clay have large surface area, and are electrically charged; hence they have high adsorptive capacity. The organic constituents include lignin resins in addition to living and dead microorganisms. The organic phase is primarily responsible for biotransformation of toxic chemicals.

The solution phase transports the pollutants through the soil matrix. The rate of movement of this phase determines the depth and extent of sub-soil and ground water pollution. Another phase and voids also play an important role in determining the permeability of the soil. In short, the following mechanisms occur in the soil-water interaction.

1. Physical Processes:
   a. molecular diffusion;
   b. dispersion;
   c. dilution; and
   d. adsorption-desorption.
2. Biochemical Processes:
   a. precipitation;
   b. oxidation-reduction; and
   c. bio-transformation.

Molecular diffusion is regarded as an instantaneous process, and is known to follow Fick's Law, and the proportionality constant in the formula is termed the diffusion coefficient. The movement of chemical from higher concentration zone to lower concentration zone occurs in direct proportion to the difference in its concentration in the two zones.

The dispersion caused by hydraulic movement is dependent on the pore size, and the movement is more in the center than near the walls. These factors coupled with separation pathway distribute the pollutants to the soil matrix by adsorption, and thus reduce the concentration in the liquid phase. The rate of dispersion is governed by the dispersion coefficient. The desorption of the chemicals may occur later.

The dilution occurs when the liquid mixes with ground water. The adsorption is believed to follow first order kinetics. It may be mathematically represented by Freundlich, Langmuir or similar type of relationships.

At times it is difficult to distinguish between adsorption and precipitation in soil-water system. The adsorptive capacity of soil depends upon:

1. grain size distribution;
2. surface area;
3. electric charge; and
4. pH.

It is known that the exchange of metal cations (Cu^{+2}, Zn^{+2}, Cd^{+2}) is affected by the presence of Na^+ and Ca^+. The competition for exchange site varies with each waste and soil.

The chemical precipitation is related to the pH of the soil. The pH of the soil can be effected by the microbial activity, and CO_2 concentration. The kinetics is also influenced by the presence of the hydrous oxides of Mn and Fe, especially the precipitation of some of the heavy metals such as Co, Ni, Cu, and Zn. The depth to which the movement of the precipitate will occur depends upon the rate and the velocity of the hydraulic flow.

The oxidation-reduction reactions reduce the complex molecular standard compounds to simple more solubilized form, thus facilitating their movement.

Bacteria in soil are responsible for transformation of pollutant. Nitrification and dentrification, nitrogen fixation and sulfur transformations are examples. The actinomycetes are very effective in transforming resistant organic compounds. Algae are capable of nitrogen fixation in soil.

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 4H^+ + 2H_2O$$

$$\underline{2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^-}$$

$$\text{overall} \quad NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

It shows that to oxidize 1 mg/ℓ of ammonia-nitrogen about 4.6 mg/ℓ of oxygen is required.

Even pesticides are microbial degraded in soil.

$$2,4\text{-}D + O_2 \xrightarrow{\text{Bacteria}} CO_2 + H_2O + C\ell^-$$

or

$$2,4\text{-}D + O_2 \xrightarrow{\text{Bacteria}} 2,4\text{-}D \text{ metabolate} + O_2$$
$$\longrightarrow CO_2 + H_2O + C\ell^-$$

Only small amounts of pesticides applied at considerably low rate can be biodegraded by soil bacteria. However, if large amounts of pesticides are applied, the probability of soil contamination, followed by leachate and ground water contamination is high.

The soil particles adsorb the chemicals from the aqueous phase (spills). These contaminated particulates can be dislodged and transported to a new location (air or water) creating a new interface. Chemicals on soil do vaporize into the air.

The equilibrium between soil-water system can be described by the general thermodynamic equilibrium correlations involving equality of chemical potentials in both phases.

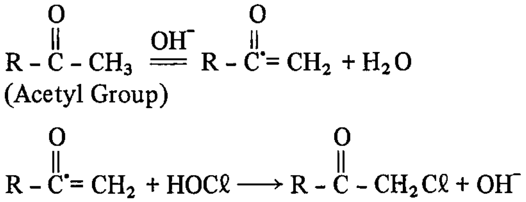
If the chemicals are discharged into the rivers and lakes as has been the case with Kepone, the pollutant is transferred to mud (benthal deposits). Partition coefficient for polychlorinated biphenyls (PCB), have been measured.

Gaseous chemical molecules in air are adsorbed on the soil, as well as are absorbed in water. Factors affecting the adsorption of gases (and liquids) on soil are:

1. moisture content;
2. water solubility;
3. chemical structure; and
4. nature of the soil.

COMPREHENSIVE CONTROL TECHNOLOGY-TRIHALOMETHANES IN ENVIRONMENT

Chlorine is added to drinking water primarily to prevent the spread of water borne diseases such as hepatitis, poliomyelitis, typhoid and cholera. However, aqueous chlorine reacts with certain precursors in water to form halogenated compounds, prominent among these are chloroform ($CHC\ell_3$), Dibromochloromethane ($CHBr_2C\ell$), dichlorobromomethane ($CHC\ell_2Br$), and Bromoform ($CHBr_3$). These trihalomethanes (THM) are suspected carcinogens-mutagens, hence their formation in water must be monitored. Trihalomethanes are formed via alternate steps of hydrolysis and halogenation of precussors [3] (e.g., acetyl group) as shown below:

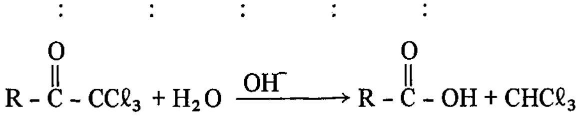


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \overset{OH^-}{=\!=} R-\overset{\overset{O}{\|}}{C^{\bullet}}=CH_2+H_2O$$

(Acetyl Group)

$$R-\overset{\overset{O}{\|}}{C^{\bullet}}=CH_2+HOC\ell \longrightarrow R-\overset{\overset{O}{\|}}{C}-CH_2C\ell+OH^-$$

A series of hydrolysis and halogenation reactions



$$\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots$$

$$R-\overset{\overset{O}{\|}}{C}-CC\ell_3+H_2O \xrightarrow{OH^-} R-\overset{\overset{O}{\|}}{C}-OH+CHC\ell_3$$

Organic compounds are emitted from combustion processes and chlorine is emitted to the atmosphere in large quantities from industrial sources. By a similar mechanism, THM's are formed in the atmosphere.

Halogenated compounds have been found in algae. $CHBr_3$ is a major constitient of *Aspayagopsis taxiformis* (red algae). In semi-quiescent water, algae settles along with other particulate matter and becomes a part of the "bottom deposits."

The Environmental Protection Agency (EPA) has recently promulgated that the total trihalomethane concentration (the arithmetic sum) in drinking water should not exceed 100 μg/l. There is no prescribed limit in the air.

Trihalomethane formation continues until the chlorine or precursor concentration is exhausted and the concentration in the drinking water continues to increase as the water moves through the distribution system. The importance of measuring the trihalomethane formation potential (THMFP) becomes significant for prediction purposes [4].

Organic constituents of surface water are subject to seasonal variation. Even day to day variations of precursor concentration in dilute aqueous solution have bearing on THMFP. We studied the THMFP under varying conditions. Figure 2

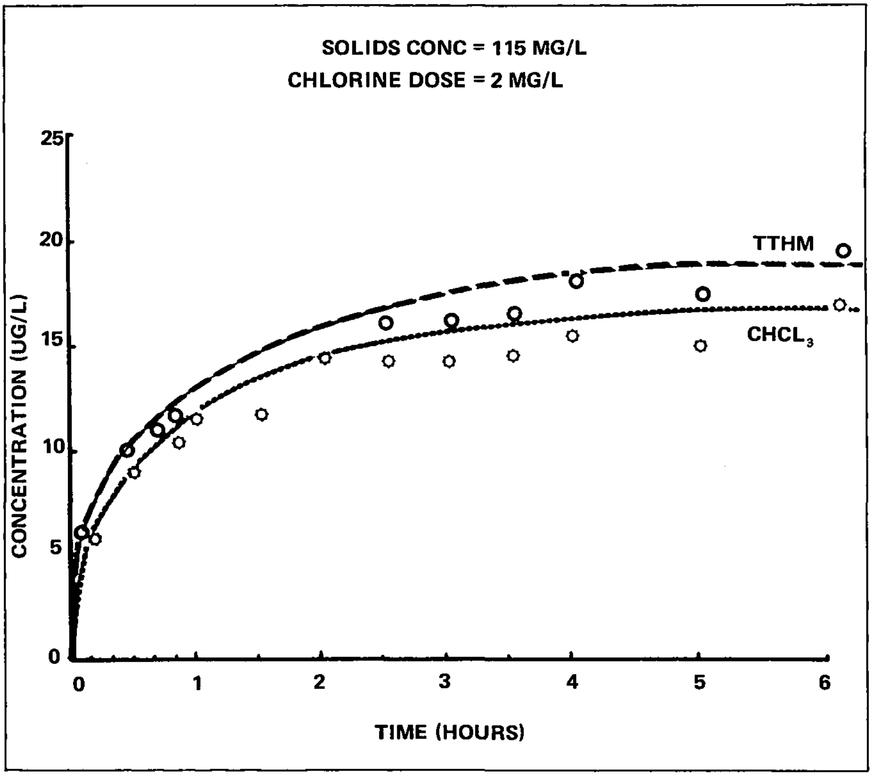


Figure 2. THM formation as a function of time.

is a typical plot of THM's at different time intervals. It indicates that $CHCl_3$ predominates. At a constant chlorine dose and fixed temperature chloroform formation increases with time and solid (precursor) concentrations as shown in Figure 3.

A kinetic analysis of reaction mechanism as outlined earlier gives the following reaction rate expression [5]:

$$\frac{d[THM]}{dt} = \frac{Ka\,[P]\,[HOCl]^2}{1 + K_b\,[HOCl] + K_c\,[HOCl]^2}$$

K_a, K_b, K_c are composite rate constants and [P] is precursor concentration.

Expressions similar to this equation are needed for other precursors present in the water sample. For practical applications a semi-empirical model is needed which would be source dependent to account for the variation in the precursor type and concentration. The simplest model to describe this situation is expressed as follows:

$$\frac{d[THM]}{dt} = K\,[Precursor]^{\alpha}\,[Chlorine]^{\beta}$$

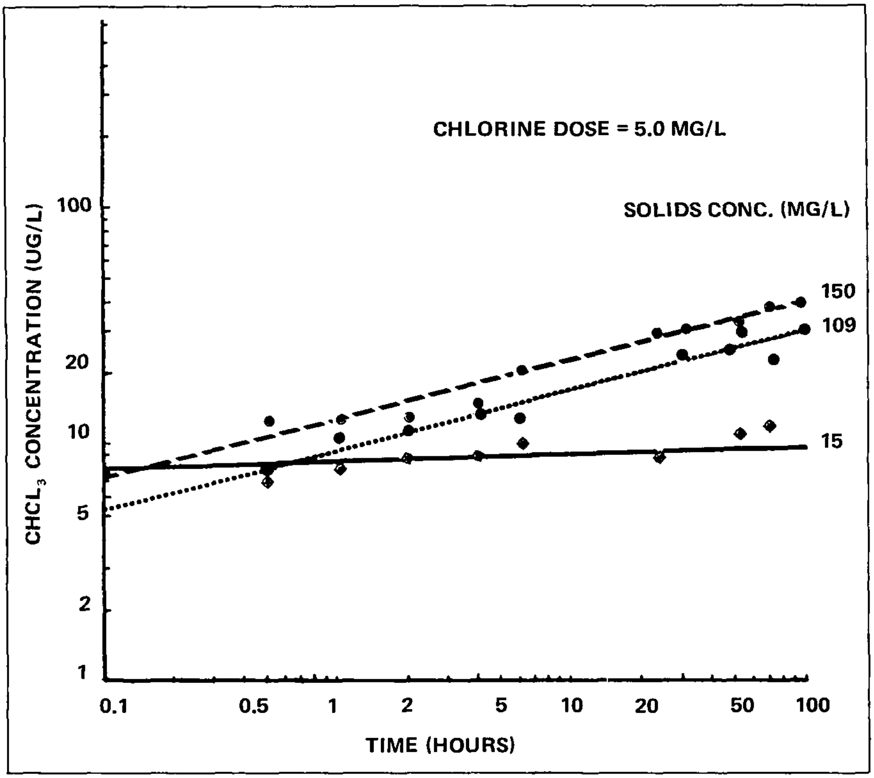


Figure 3. CHCL$_3$ concentration as a function of solids concentration.

Trihalomethane Removal

The THM's in water can be removed either by removing the THM's after they are formed or by controlling the precursors before chlorination. Alternatively the chlorine can be replaced by another chemical such as ozone or chlorine dioxide. But we do not recommend that any other chemical should replace chlorine until it has been as vigorously and extensively tested as chlorine. One method for removing THM's or THM-Precursors is by adsorption on Granulated Activated Carbon (GAC). The economics of the process depends on the cost and the efficiency of regeneration of GAC. The spent carbon is regenerated at high temperatures (> 1650°F) and the retention time varies from five to twenty minutes. The typical removal rates of THM's and THM-Precursors on GAC are depicted in Figure 4. In the EPA study [6] the average THM reduction rate for the first two weeks was close to 100 per cent. In about seven to ten days after that it leveled off at about 43 per cent. In our study on THM-Precursor removal [7], the virgin carbon in the first two weeks removed THMFP on an average of 80 per cent. In the seventh week the THMFP reduced to about 50 per cent.

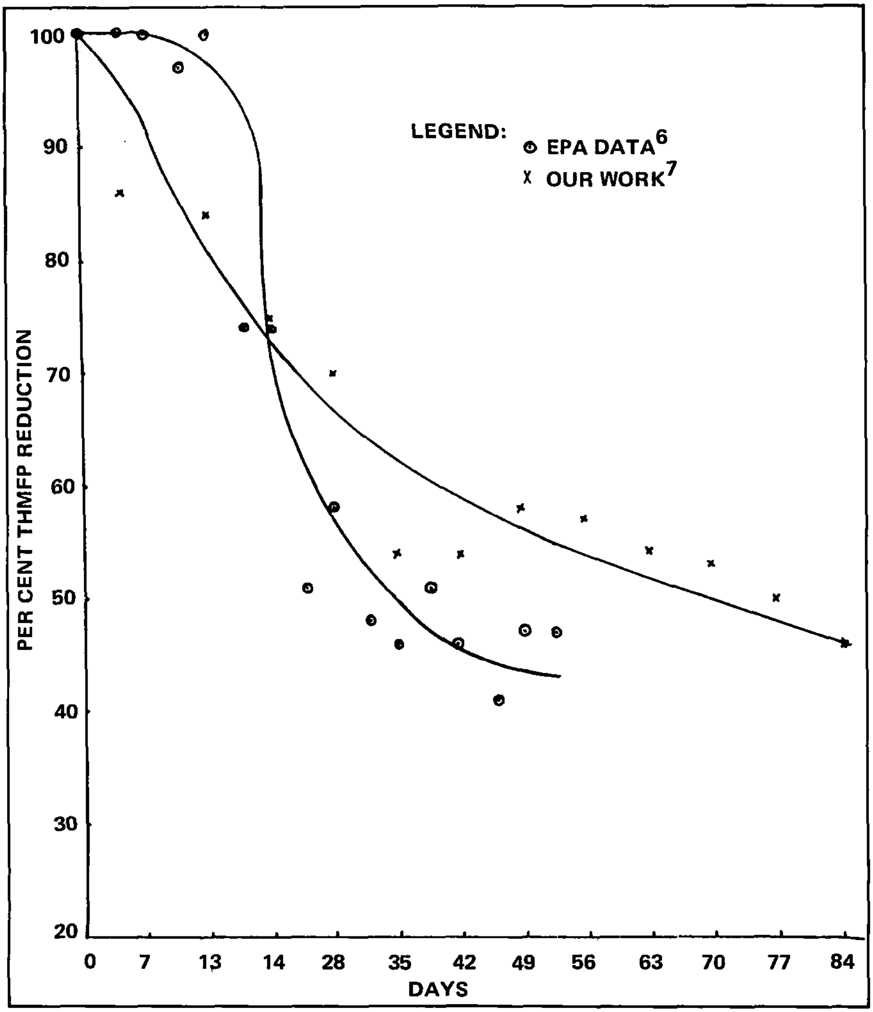


Figure 4. Per cent reduction in THM formation in finished water after passing through a 3-foot GAC column.

Except for small differences in the removal efficiencies in the first two weeks, THM-Precursor removal appears to be a better solution for THM reduction in drinking water. If THM's are removed, then on regeneration, these are volatilized as such into the atmosphere and they still remain in the ecosystem. Thus we have transferred the problem from one subsystem to the other. On the other hand, if THM-Precursors are removed, the regeneration processes are expected to emit mostly CO_2 and H_2O – non pollutants.

For every pollutant or a set of pollutants, we need to go through a comprehensive system analysis which leads to a total reduction of these pollutants in the ecosystem rather than a shift in the problem. Thus, pollution control technology of the future should be oriented towards a comprehensive long range optimal solution.

REFERENCES

1. Environmental Protection Agency, *Acid Rain,* EPA-600/9-79-036, July 1980.
2. L. J. Thibodeaux, *Chemodynamics,* John Wiley and Sons, New York, 1979.
3. J. C. Morris, *Formation of Halogenated Organics by Chlorination of Water Supplies,* Environmental Protection Agency, EPA-600/1/75/008, 1975.
4. A. A. Stevens and J. M. Symons, Measurement of Trihalomethanes and Precursor Concentration Changes, *J. AWWA, 69,* p. 546, 1977.
5. M. M. Varma, R. C. Chawla, A. Balram, and H. M. Katz, Trihalomethane Formation in Lyophilized Potomac Water, *Water-1980,* AIChE Symposium Series, S-209, New York, 1981.
6. Environmental Protection Agency, *Removing Potential Organic Carcinogens and Precursors from Drinking Water, Vol. I,* EPA-600/2-80-130a, August 1980.
7. M. M. Varma, R. Parsuram, and T. A. Stumm, *Measuring the Efficiency of Regenerated Carbon – A Pilot Plant Study,* Washington Suburban Sanitary Commission, Hyattsville, Maryland, 1980.

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